ACTIVE SITES IN ZEOLITES. DEALKYLATION AND DEHYDRATION ON ALKALINE EARTH-Y ZEOLITES

By
N. PESL and H. NOLLER
Institute for Physical Chemistry of the Technical University, Vienna

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Dealkylation of 2-butylbenzene and dehydration of 2-butanol were studied on MgY, CaY and BaY zeolites of different water content, using temperature programmed desorption (TPD) and microcatalytic technique. The dealkylation on MgY and CaY was considerably increased when water was added, whereas that on BaY was independent of water content. On MgY and CaY the TPD maxima (of benzene) were shifted to lower temperatures, when water was added, indicating a higher cracking activity. Two maxima appeared on CaY. The dehydration of 2-butanol was studied only on MgY and found to be independent of water content.

Introduction

It is well known that very active cracking catalysts show high acidity. Three kinds of acidic centers have been discussed:

a) Protons of OH groups, originated through the interaction of cations with water molecules (Brönsted acidity)

$$Me(OH_2)^{2+} \rightarrow MeOH^+ + H^+ \qquad (1)$$

b) Tri-coordinated Al atoms (Lewis acidity) with high electron pair acceptor (EPA) strength

c) Cations accessible to the reactant (Lewis acidity).

With IR spectroscopic methods, WARD [1] has found Brönsted acidity to have a maximum between 450 and 600° C and decreases steeply at higher temperatures. The Lewis acidity mentioned in *b)* has been found to increase and to be much more pronounced, within the temperature range of 700—800° C, than Brönsted acidity.

NOLLER [2] has suggested cations to be indispensable active centers for reactions on polar catalysts. The interaction between an EPA site (cation) of the catalyst and an EPD (electron pair donator) site of the reactant (leaving group OH or C_6H_5 in this study) is assumed to be essential for the catalytic activity.

The purpose of this study is to contribute to the question concerning the nature of the active centers. The temperature programmed desorption (TPD) and the microcatalytic technique were used. The dependence of activity upon the content of water and the percentage of exchange was studied. Catalytic results were compared with the TPD caracteristics of samples subjected to treatments as similar as possible.

Experimental

The starting material was a NaY zeolite (SK 40) from Union Carbide. The cation exchanged zeolites were prepared by treating this sample with 0.1 n solutions of the cation to be introduced for 3 h at 90° C. The anions were chlorides.

For TPD, the catalysts were activated at 540° C for 15 minutes in a reactor of quartz glass evacuated to 13 Pa, and cooled to room temperature. The zeolites treated in this way are denominated 'anhydrous. Secondary butyl benzene (SBB) was injected through a septum (and adsorbed). The pressure was always adjusted to 10 000—13 300 Pa. After 3—5 minutes the reactor was again evacuated for some minutes in order to remove weakly adsorbed species. Then the catalyst was heated with a rate of 50° C/min. The desorbing substances were detected in a quadrupol mass spectrometer connected to the reactor. The reactor was also connected, through a valve, to a vacuum pump. To prevent water from diffusing back through the vacuum pump to the zeolite, a liquid air trap was placed between the valve and the pump. The valve was heated to 70—80° C to prevent condensation of water.

The masses 78 (representative for benzene) and 77 (representative for SBB) were continuously recorded. A somewhat larger mass range was cyclically covered by the mass spectrometer. Water was injected before introduction of SBB to study its influence. The figures given in the spectra and tables indicate the amount of water injected per weight of catalyst.

For the microcatalytic technique (dealkylation of SBB, dehydration of 2-butanol) the zeolites were similarly activated at 540° C for 15 min in a He carrier gas flow, previous to reaction. The elution of the reaction products and the non-converted reactant was observed with a thermal conductivity detector and recorded. At the maximum of the elution process, 0.3 ml gas was taken out with a gas syringe and injected into a gas chromatograph with a 1.3 m Carbowax 1540 on Teflon 20—60 mesh column and an FID. For studying the effect of water a measured quantity was injected to the catalyst, previous to the reactant.

Results and Discussion

Temperature programmed desorption

Catalysts studied: Ca_{40}-Y, Ca_{58}-Y, Ca_{100}-Y, Mg_{32}-Y and Mg_{62}-Y (subscript: degree of exchange in percent of Na^+ ions exchanged).

Ca_{40}-Y did not show cracking activity for SBB, not even after treatment with water (Fig. 1). The only substance desorbed (at 300° C) was SBB. All Ca^{2+} ions are located on SI sites, where they are not accessible to the reactant and hence inactive. (The appearance of mass 78 in the mass spectrum does not indicate formation of benzene, but corresponds to the mass spectrum of SBB.)

Anhydrous Ca_{58}-Y gave a desorption maximum of benzene at 480° C. It was shifted to 475° C, when a small amount of water was injected, and a second maximum of benzene appeared at 375° C (Fig. 2).

In our opinion, the cracking activity should not be ascribed to Brönsted sites, for several reasons: The anhydrous zeolite exhibited activity. If this was due to some remaining Brönsted sites, the maximum at 480° C should be increased on adding

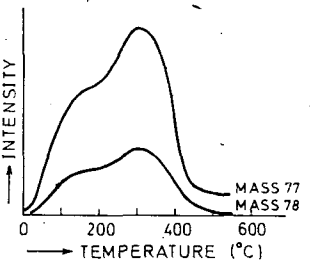

Fig. 1a. TPD spectra on anhydrous Ca_{40}-Y

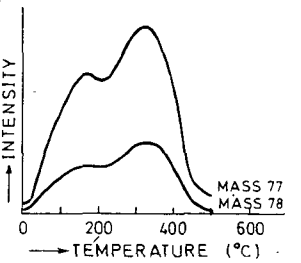

Fig. 1b. TPD spectra on Ca_{40}-Y with 1.8 weight % H_2O

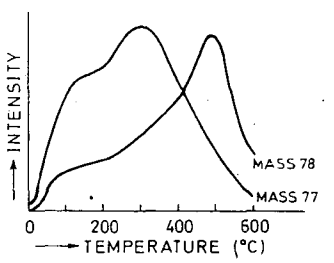

Fig. 2a. TPD spectra on anhydrous Ca_{58}-Y

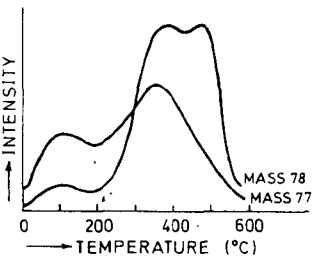

Fig. 2b. TPD spectra on Ca_{58}-Y with 6.5 weight % H_2O

water, but a second maximum should not appear. Provided there are no Ca^{2+} ions on SII sites until all SI sites are occupied, the occupation of SII sites in CaY should begin at an exchange of 57%. Hence in anhydrous Ca_{58}-Y, only a few Ca^{2+} ions should be on SII sites. The cracking activity may be ascribed to them, *i.e.* the maximum at 480° C is due to the interaction of SBB with waterfree cations in accessible sites.

The "catalytic" function of water would be to enable the cations to migrate [3] from the SI sites (where they are located in the anhydrous zeolite without displaying activity) to the SI′ and SII′ sites or even SII sites, where they exhibit activity, rather than originate Brönsted sites (equation 1). Thus, the 480° C maximum could be ascribed to the desorption of benzene, previously formed from SBB, from an anhydrous cation. A hydrated cation is less strong an adsorption site, but is still active for cracking. So benzene is desorbed at 375° C.

It would be difficult to explain this result with OH groups. It is true, the number of OH groups should increase, when water is added (equation 1). But this should enhance the maximum or bring about a continuous shift to somewhat lower temperatures rather than lower the temperature by 100° C. It would be difficult to assign the two maxima to two types of OH groups, in the same way as we assign it to anhydrous and hydrated cations.

In Mg_{32}-Y, 9 of 16 SI sites are occupied. The anhydrous zeolite had a small maximum of benzene at 380° C (Fig. 3). When water was added a strong well marked maximum of benzene appeared at 360 °C. Mg_{62}-Y was similar to Mg_{32}-Y.

The maximum found with the Mg-Y was close to the low temperature maximum of Ca-Y. There was no second maximum. Mg^{2+} is known to be considerably more active than Ca^{2+} in comparable catalysts [4]. On the other hand, it retains more water. The reason for the activity and the retention of water is the same, *i.e.* its high EPA strength. So it is possible that the high temperature maximum observed with Ca-Y

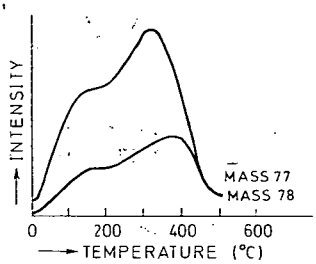

Fig. 3a. TPD spectra on anhydrous Mg_{32}-Y

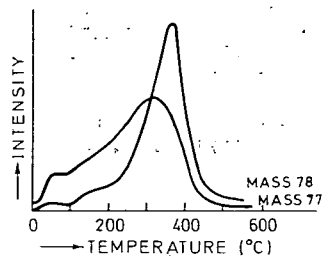

Fig. 3b. TPD spectra on Mg_{32}-Y with 3.1 weight % H_2O

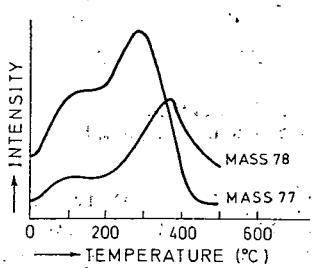

Fig. 4a. TPD spectra on anhydrous Mg_{62}-Y

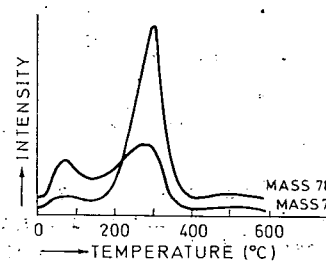

Fig. 4b. TPD spectra on Mg_{62}-Y with 4.0 weight % H_2O

cannot be seen with Mg-Y, because it is impossible to remove the water to as high an extent as in Ca-Y.

With higher content of water the desorption maxima of benzene were shifted to lower temperatures.

Microcatalytic technique, Dealkylation

SBB was studied on Ca_{100}-Y and Ba_{64}-Y (Tables I and II). The cracking activity of Ba_{64}-Y was nearly as high as that of Ca_{100}-Y. In our opinion, there is no possibility to interpret this finding with Brönsted sites, since Ba-Y is known to have fewer Brönsted sites than Ca-Y [5]. Thus, ascribing the activity to Brönsted sites, we should expect Ca_{100}-Y to be more active than Ba_{64}-Y. However, the result can be explained if cations are assumed to be active sites. As Ba^{2+} tends to occupy SI′ and SII′ sites rather than SI sites [6], Ba-Y samples with a lower degree of exchange can have a higher activity than Ca^{2+} exchanged samples.

Table I

Dealkylation of SBB *on* Ca_{100}-Y *as a function of content of water and temperature*

Tempera-ture of reaction °C	Water injected weight %	Aliphatic hydrocarbons %[a]	Benzene %[a]	SBB %[a]
500	0	28	22	50
	0.41	33	23	44
	2.07	35	30	35
420	0	23	11	66
	0.41	33	20	47
	2.07	38	12	50
330	0	23	13	64
	0.83	22	14	64
	4.15	27	19	54

[a] The peak areas are given so that the sum of them is equal to 100%. No correction for sensitivity of different species was applied.

Table II

Dealkylation of SBB *on* Ba_{64}-Y *as a function of water content and temperature*

Temperature of reaction °C	Water injected weight %	Aliphatic hydrocarbons %[a]	Benzene %[a]	SBB %[a]
500	0	29	24	47
	2.22	30	26	44
440	0	20	16	64
	2.22	19	18	63
350	0	20	13	67

[a] The peak areas are given so that the sum of them is equal to 100%. No correction for sensitivity of different species was applied.

Microcatalytic technique, Dehydration of 2-butanol

Mg_{32}-Y was studied between 330 and 540° C (Table III). Only a small alteration of the conversion was observed in that temperature range (of 210° C).

This may again be related to the migration under the influence of water of Mg^{2+} from inactive SI sites in the prisms to the (active) SI′ and SII′ sites in the cubooctahedrons. A higher temperature implies a higher rate of reaction. If one (invariable) active center (one cation) is considered only the highest conversion should be expected at 540° C. However, in the reaction water is produced and that varies the number of Mg^{2+} in accessible positions, *i.e.* the number of active sites. Since less water is retained on the zeolite at higher than at lower temperatures, the number of the cations in active sites decreases with increasing temperature.

Table III

Dehydration of 2-butanol on Mg_{32}-Y *as a function of content of water and temperature*

Temperature of reaction °C	Water injected weight %	Aliphatic hydrocarbons $\%_{a)}$	2-butanol $\%_{a)}$
540	0	64	36
400	0	67	33
	1.81	66	34
	3.62	68	32
330	0	69	31
	1.81	69	31
	3.62	68	32

$_{a)}$ The peak areas are given so that the sum of them is equal to 100%. No correction for sensitivity of different species was applied.

Consequently, there are two opposite effects: the increase of the rate of reaction on one hand and the decrease of the number of active sites, because of the lower water content on the other hand. This may be the reason for the reaction rate found to be independent of temperature.

References

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